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13. ABSTRACT (Maximum 200 words) The preparation of N-phenyl-substituted poly(isocyanide) (N- ϕ -PIM) utilizing a Ni(II) catalyst in methanol yields a brown material having a number average molecular weight of about 2000. Analysis of this "as prepared" polymer indicates that a rigid rod structure is present in the derived solid. Dissolution of this "as prepared" N- ϕ -PIM in halocarbon solvents or THF apparently leads to unraveling of the helical polymer with subsequent aggregation and precipitation of materials that have different properties from the original. These processes have been investigated by NMR, GPC, and light scattering techniques in THF and other solvents. UV spectroscopy has been utilized to follow the kinetics of the aggregation process in solution. X-ray diffraction (XRD) measurements have been employed to investigate the changes attendant with precipitation. An explanation of these observations is offered that implicates the uncoiling of the rigid rod helix as the most important step in defining subsequent physical and chemical properties of the ultimate amorphous polymer.				
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Aggregation Kinetics and Precipitation Phenomena in Poly(phenyl- isocyanide)

FINAL REPORT

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Abstract

The preparation of N-phenyl-substituted poly(isocyanide) (N- ϕ -PIM) utilizing a Ni(II) catalyst in methanol yields a brown material having a number average molecular weight of about 2000. Analysis of this "as prepared" polymer indicates that a rigid rod structure is present in the derived solid. Dissolution of this "as prepared" N- ϕ -PIM in halocarbon solvents or THF apparently leads to unraveling of the helical polymer with subsequent aggregation and precipitation of materials that have different properties from the original. These processes have been investigated by NMR, GPC, and light scattering techniques in THF and other solvents. UV spectroscopy has been utilized to follow the kinetics of the aggregation process in solution. X-ray diffraction (XRD) measurements have been employed to investigate the changes attendant with precipitation. An explanation of these observations is offered that implicates the uncoiling of the rigid rod helix as the most important step in defining subsequent physical and chemical properties of the ultimate amorphous polymer.

Introduction

Polymers that form when organoisocyanides are polymerized have been studied since the 1960s.¹ Much of the work that has been done during the intervening thirty years has been based on the assumption that these polymeric materials are rigid rod entities having a helical molecular structure.² Thus, many of the arguments that explain the physical properties and chemical reactivity of these polymers have assumed that rigid rods are always present in these systems.³ Cracks in this facade have begun to appear, however, because, while the sterically hindered representatives of these polymers are undoubtedly helical,⁴ less steric hinderance in the attendant substituent group has produced results that can best be interpreted if rigidity of the helix is not strictly maintained.^{3b,5} Recently we reported that the phenyl substituted representative of this group of materials displays an ¹⁵N NMR spectrum having more than two clearly defined, but closely spaced, resonance manifolds⁶ and so we concluded that N-φ-PIM (an abbreviation we use based on the N-phenylpolyimine nomenclature⁷) has a random coil structure.

The present report focuses attention on the aggregation and precipitation kinetics and properties of solutions of N-φ-PIM. Original reports⁸ dealing with this polymer concluded that it was insoluble in most solvents. We have discovered that low molecular weight examples of N-φ-PIM have considerable solubility in halocarbon (CH₂Cl₂, CCl₄) and ether (THF) type solvents. While these solutions can be examined using classical spectroscopic methodology during brief periods of time after preparation (hours), longer periods of time (days) lead to aggregation of the polymer chains and ultimately precipitation. Our data are best interpreted if N-φ-PIM is not a purely helical polymer in solution and we thus concur with Hong and Fox⁹ when they state that "sterically unhindered polyisocyanides probably exist as random coils...", at least in solution.

We have studied the solution chemistry of N-φ-PIM by UV spectroscopy, GPC, and light scattering in a number of solvents. All of these techniques show that over the course of days to weeks (depending on the temperature) N-φ-PIM aggregates and then precipitates. Further, we have used X-ray diffraction (XRD) to investigate the structural changes in the solids isolated, as a function of time, when converting solutions of the "as prepared" polymer to the ultimate precipitate. Our conclusion is that the "as prepared" polymer has a rigid rod structure which slowly converts to a random coil structure with time in solution.

Experimental

Materials - Trichloromethylchloroformate (diphosgene) was purchased from Lancaster Synthesis, Inc. while all other reagents were obtained from Aldrich Chemical Co. All solvents were distilled prior to use. Anhydrous nickel chloride was prepared from NiCl₂·6H₂O by treatment with SOCl₂ followed by filtration of the yellow solid. Phenylisocyanide was prepared from N-phenylformamide using the procedure described in the literature.¹⁰ Phenyl isocyanide is a liquid that can be easily vacuum transferred at room temperature and 0.5 mm Hg to a receiver cooled to -20 °C. Pure phenyl isocyanide is colorless but rapidly begins to turn green upon coming into contact with air. As a consequence, polymerization reactions were always done on freshly prepared and distilled samples of phenylisocyanide (φNC).

Procedures - The polymerization of ϕNC was carried out using a slightly modified method to that described in reference 8. Freshly distilled ϕNC was added to a stirring mixture of anhydrous NiCl_2 in anhydrous methanol. The mole ratio of reactant to catalyst was usually 100:1 and the amount of solvent was dictated by the amount of ϕNC utilized (50 mg ϕNC /1 mL MeOH). After stirring for one week, the polymer was removed from the supernatant liquid by filtration and the solid polymer was then washed with methanol until the washings were colorless. The resultant brown solid polymer was dried *in vacuo* and labeled "as prepared". Elemental Analysis: Calc. for $(\text{C}_7\text{H}_5\text{N})_x$; C, 81.53%; H, 4.89%; N, 13.58%; Found; C, 80.27%; H, 5.24%; N, 13.13%.

Solubilization of the "as prepared" polymer was most easily achieved in THF or CH_2Cl_2 . For instance, 1 mg of the "as prepared" polymer was completely soluble in 1 mL of either solvent by simply shaking for 5 to 10 min; quicker dissolution could be obtained by ultrasonication. Supersaturated solutions of the polymer in THF could be prepared by shaking an excess of the "as prepared" polymer with THF (~100 mg/10 mL THF) for 5 min and then filtering off the remaining solid. These supersaturated solutions begin to precipitate a yellow-brown solid after 20-30 min at room temperature and precipitation is complete after 24 hours. Elemental Analysis: C, 76.47%; H, 5.25%; N, 11.16%. Addition of methanol to a THF solution that was freshly prepared as described above causes rapid precipitation of a yellow-brown solid that can be isolated by filtration and has identical physical and spectroscopic properties as the "as prepared" polymer. Elemental Analysis: C, 80.49%; H, 5.35%; N, 12.86%.

Instrumentation and Measurements - Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 1650 FTIR spectrometer between 400 and 4000 cm^{-1} . UV-Vis spectra were obtained in 1 cm quartz cells using a Perkin-Elmer $\lambda 2$ spectrometer between 800 nm and the solvent cutoff. Kinetic measurements were made by monitoring the solution absorbance at 350 nm. Solutions were prepared with varying concentrations (ranging from 0.1 to 1 mM in repeat unit), put in a constant temperature water bath at a selected temperature (ranging from 25 - 42 $^{\circ}\text{C}$), and then filtered through a 0.45 μm frit before each measurement. Time dependent data were fit to a pseudo first order equation using the fitting routines in SigmaPlot (v. 2.0, Jandel Corporation).

Molecular weights were estimated by GPC using a series of Ultrastyrigel columns (500, 10^3 , and 10^4 Å, Waters) attached to a Perkin-Elmer 1020 LC Plus liquid chromatography system connected to a Waters 712 WISP autosampler. The autosampler allowed the use of polystyrene standards for every set of samples run. Typically, an "as prepared" polymer was dissolved in either THF or CH_2Cl_2 , a weighed amount of a narrow molecular weight polystyrene was added to the solution as an internal standard, filtered through a 0.45 μm frit, and then stored at room temperature. After various amounts of time, aliquots were withdrawn, refiltered through the 0.45 μm frit, and then the chromatogram determined.

NMR spectra were obtained on a Bruker AM300 spectrometer at 75 MHz for ^{13}C and 30 MHz for ^{15}N in appropriate deuterated solvents on doubly labeled "as prepared" polymer, $(\phi^{15}\text{N}^{13}\text{C})_x$. For the ^{13}C spectrum, 12 mg of the polymer was dissolved in a mixture of 0.8 mL CCl_4 and 0.2 CDCl_3 , placed in a 5 mm tube, and the spectrum determined (this took 20-30 minutes). For ^{15}N , the same sample was transferred to a 10 mm tube so that as precipitation occurred

on the overnight runs, the precipitating sample solid floated to the top of the liquid and out of the probe.

Particle sizes were determined by dissolving 10 mg of the "as prepared" polymer in 10 mL of THF, filtering the solution through a 5.0 μm filter plug into a 1.0 \times 1.0 cm quartz cell, and utilizing a Brookhaven Instruments Corporation Model BI-90 Particle Sizer. The samples were stored at room temperature and aliquots were taken once a day, refiltered through the 5.0 μm frit, and the particle size distribution of the remaining sample in solution determined.

The XRD spectra were found by suspending the "as prepared" polymer in methanol, then suction filtering through a silver frit sample holder, washing methanol through the sample to obtain a uniform layer, and then using a Scintag XDS 2000 θ - θ Powder X-ray Diffractometer (Cu/K α , 1.54184 \AA , 45 kV, 40 mA, scan rate = 2.0 $^\circ/\text{min}$, scan range = 0 - 34 $^\circ$) for determinations. For the effect of precipitation, 20 mg of the "as prepared" polymer was dissolved in 20 mL of THF, filtered through a 0.45 μm frit, and stored at room temperature. Aliquots were taken at various times, evaporated *in vacuo*, and the solid residue was prepared for the XRD measurement as described above.

Results

Preparation and Characterization of N- ϕ -PIM. The N-phenyl-substituted polyimine used in this study was synthesized in the usual manner by reacting and stirring phenylisocyanide with anhydrous NiCl_2 (the mole ratio of ϕNC to NiCl_2 was usually 100/1) in methanol for several days.⁶ Filtration of this "as prepared" polymer from the supernatant liquid mixture yielded a dark brown solid which could be solubilized in several different solvents and then reprecipitated by adding methanol to yield a dark yellow-brown solid. The apparent number average molecular weight of these materials, as determined by GPC using polystyrene standards, was usually approximately 2000. However, if a small amount of the "as prepared" polymer was dissolved in a large amount of methanol, a large excess of fresh ϕNC added, and then stirred for several days (with no added NiCl_2), a yellowish brown polymer could be precipitated having a number average molecular weight higher than the original. Analysis of all these derived solids by GPC always revealed a very low molecular weight component in addition to the major polymeric entity.¹¹ (As we will show later, apparently higher molecular weight examples of N- ϕ -PIM can be prepared by a slow precipitation route but these precipitates are insoluble in all solvents.) Elemental analyses of these polymers revealed the presence of nickel and chlorine (NiCl_2 stoichiometry) but we have yet to determine the nature of the bonding of the nickel atoms that are present in these polymers.¹²

The N- ϕ -PIM sample of molecular weight 2000 is most soluble in solvents such as THF and common halogenated solvents like CH_2Cl_2 , CHCl_3 , and CCl_4 . Dissolution of doubly labelled N- ϕ -PIM (synthesized from 100% isotopically substituted isocyanide, $\phi^{15}\text{N}^{13}\text{C}$) in an 80:20 mixture of CCl_4 : CDCl_3 gave the NMR spectra in the imine region shown in Figure 1. As can be readily seen, while the ^{13}C NMR spectrum exhibits two imine resonances in close proximity, the ^{15}N NMR spectrum clearly displays at least three distinct resonances. These NMR spectra must be determined in a short window of opportunity after the initial dissolution because the solution

begins to precipitate solids which distort the spectral acquisition. Solid state NMR spectra, either ^{13}C or ^{15}N , show only a single peak in the imine region because of linewidth considerations.

Examination of N- ϕ -PIM materials rapidly precipitated from solution, from a variety of solvents, are nearly identical in all of their physical characteristics to the "as prepared" materials and are consistent with the properties described in the literature.^{2d} However, the IR spectra of these different materials do have subtle differences which can be attributed to occlusion of the solvent upon precipitation of the N- ϕ -PIM. Simple washing with methanol removes the entrapped solvent while prolonged evacuation of the solid under dynamic vacuum is not nearly as effective in removing these occluded solvents. Slow precipitation of N- ϕ -PIM from more dilute solutions yields very different behavior as we will show below.

Examination of the "as prepared" solid polymer by XRD (Figure 2) indicates that the bulk of the material has rigid rod character. The predominant feature in these "as prepared" solids occurs at 11.5 Å with an attendant amorphous halo centered at approximately 4.5 Å.¹³

Aggregation and Slow Precipitation Phenomena. Dissolution of N- ϕ -PIM in THF or CH_2Cl_2 produces a yellow solution that is reasonably stable if the concentration is kept low but after a few days precipitation occurs. For example, if 1 mg of N- ϕ -PIM is dissolved in 1 mL of CH_2Cl_2 visual evidence of precipitation is evident after 2 to 3 days. GPC analysis of this solution initially reveals an asymmetric band with a retention volume similar to that of polystyrene standards with $M_n \sim 2000$ and an accompanying band at longer retention time corresponding to a very low molecular weight entity. Daily filtration of this solution through a 0.45 μm filter and then analysis of the filtrate by GPC gives the results shown in Figure 3. The $M_n \sim 2000$ band becomes more symmetric with time (the maximum shifts slightly towards longer retention time) and decreases in intensity with respect to the internal standard. The band associated with the very low molecular weight species also decreases in intensity with time. Finally, a new band at shorter retention time (retention volume associated with polystyrene of $M_n \sim 80,000$) slowly increases in intensity, although this band never achieves great prominence. Qualitatively, the buildup of this short retention time band is in agreement with the more rigorous kinetic analyses described later in this paper.

Analogously, N- ϕ -PIM dissolved in THF (1 mg in 1 mL) was examined by light scattering techniques. The solution was filtered daily through a 5.0 μm filter and the average particle size in the filtrate determined. As shown in Figure 4, the particle size grew dramatically as the aggregation occurred (filtration through a 0.45 μm filter did not show these increases since the particle size exceeds the filter pore size) and the rate of the increase in the diameter of the dissolved particles is again qualitatively in agreement with the kinetic results obtained from our UV analysis.

Confirmation that the "as prepared" polymer, as isolated from the synthesis, and the precipitated polymer, as isolated after dissolution, are different comes from the XRD results. The originally formed polymer exhibits a single diffraction peak at 11.5 Å and a diffuse, broad band centered around 4.5 Å (Figure 2). This is the type of XRD pattern found for rigid rod polymers.¹³ Dissolution in THF solvent and subsequent slow precipitation produces a solid with an XRD

pattern with broad peaks that appear to be centered at 14 Å and in the 3-6 Å region which is consistent with an amorphous polymer precipitate.¹³ This result seems to indicate that the original rigid rod conformation is undergoing a change to a random coil conformation prior to the ultimate aggregation and precipitation that occurs slowly.¹⁴ The relative changes of the intensities of the various XRD peaks as a function of time is shown in Figure 5.

UV-vis Kinetic Analysis of the Aggregation Phenomena. The UV-vis spectrum of a typical N-φ-PIM sample in (solvent) is shown in Figure 6. The primary absorptions are broad, intense, and essentially featureless (for example, the molar absorptivity at 350 nm is about 1000 L-cm/mol repeat unit for all solvents and at all temperatures investigated). This is consistent with π - π^* transitions of strongly interacting orbitals, i.e. the electronic structure of these polymers should be interpreted in terms of band theory, as previously suggested.^{2c} However, close examination of the absorption onset reveals a weak shoulder centered at about 550 nm. Simulations indicate that this shoulder is relatively narrow and is consistent with an n - π^* type transition. This is in agreement with the Extended Hückel calculations of Kollmar and Hoffman^{2c} which show the highest occupied band to be a nitrogen lone pair.

The time dependence of the concentration of N-φ-PIM in a number of solvents was monitored by UV-vis spectroscopy at a number of temperatures. The solutions were thermostatted at a given temperature and aliquots were removed periodically, filtered through a 0.45 μm filter, and the UV-vis spectrum recorded. The reaction of the polymer in solution follows simple pseudo-first order kinetics at all temperatures and in each of the solvents employed (THF, CH₂Cl₂, and CCl₄). Results for THF are shown in Figure 7 and similar behavior was found for the other solvents. The observed rate constants, k_{obs} , change linearly with concentration. This is consistent with a group transfer process¹⁵ so that the slopes of the lines in Figure 7 give the intrinsic rate constant, k . The temperature dependence of k followed Arrhenius behavior and gave activation energies of 51 kJ/mol for THF, 44 kJ/mol for CCl₄, and 70 kJ/mol for CH₂Cl₂.

Discussion

The ¹⁵N NMR spectrum of N-φ-PIM indicates that it cannot be a simple helical, rigid rod polymer in solution. In other polyisocyanides, two ¹³C resonances have been observed⁵ (similar to our spectra) and this has been attributed to syn-anti isomerization of the imine bond along the macromolecular backbone. However, this cannot account for three ¹⁵N imine resonances and we do not believe that it is responsible for any of our observations. To a first approximation there are no syn or anti isomers because the substituents at the carbon atoms are the same. Thus, in this context, syn or anti indicates the orientation of the phenyl groups relative to the helicity of the backbone. We would not expect that the NMR resonances for these two types of stereoisomers to exceed the linewidths for these polymer systems. Further, at a site where an imine bond changes from syn to anti there would be a large steric repulsion between neighboring phenyl groups which would make such an isomerization along a given chain unlikely. Instead, we propose that the NMR spectra arise from conformational changes along the C-C backbone, as demonstrated in Figure 8. The helical conformation arises from C-C bonds in the *s-cis* geometry; if, in solution, these bonds isomerize to an *s-trans* geometry then a considerably different structure arises which has several important consequences. First, three chemical shifts in the NMR should

be observable and easily resolvable: an *s-cis* domain, an *s-trans* domain, and a transition domain (or the domain wall between the *s-cis* and *s-trans* regions). Second, the *s-cis* segment will be helical while the *s-trans* region is likely to be linear. The transition domain is a segment where the structure changes between helical and linear, probably requiring several repeat units. Finally, in order for this to be a viable proposal, the energy difference between the structures must be relatively small; Kollmar and Hoffmann^{2c} estimate this to be about 25 kJ/mole repeat unit. Even given the errors expected from an Extended Hückel calculation and the unaccounted for role of solvation, it is not unreasonable for these structural motifs to exist in solution.

This model for the polymer structure can also account for the apparent molecular weight change observed in the GPC; rather than a molecular weight change we are simply measuring a change in the hydrodynamic volume of the polymer (which is, of course, what the GPC experiment actually samples) as the aggregation occurs. This explanation is bolstered by the XRD results that show the change from a rigid rod structure to an amorphous, presumably random coil, structure as the precipitation occurs. The "as prepared" polymer slowly loses its initial helical character which then allows for the subsequent aggregation and precipitation of an amorphous product and this process is solvent dependent although the details of the solvent interactions have not been established.

Conclusion

The preparation and isolation of many polymers is routinely followed by purification of the polymer so that meaningful characterization of the material can be done. Our results show that in some situations the purification process, which usually involves dissolution of the polymer followed by reprecipitation, can alter the molecular and structural characteristics of the original preparation. While the dissolution of a polymer, and subsequent conformational changes, are certainly time dependent the structural architecture, and its integrity, can differ depending on the phase in which the polymer is ultimately immersed. Caution must be exercised when manipulating polymeric entities since the treatment regimes utilized can lead to vastly different materials with vastly different physical and chemical properties.

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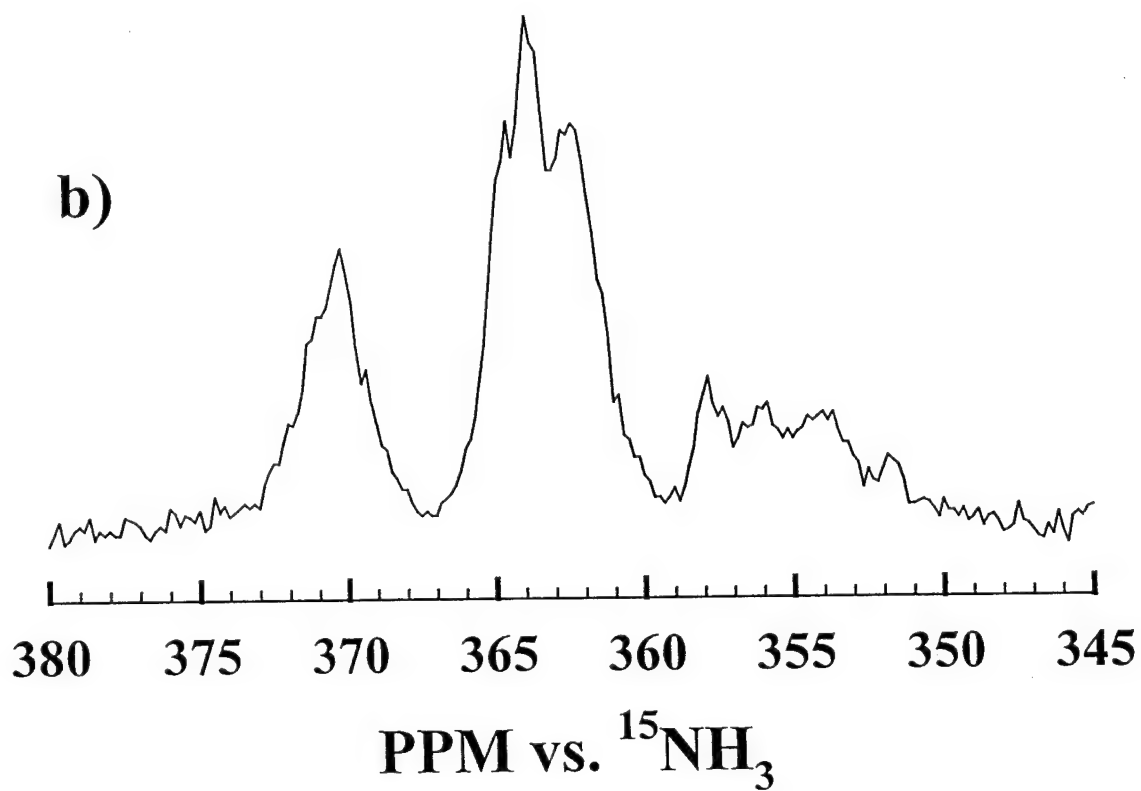
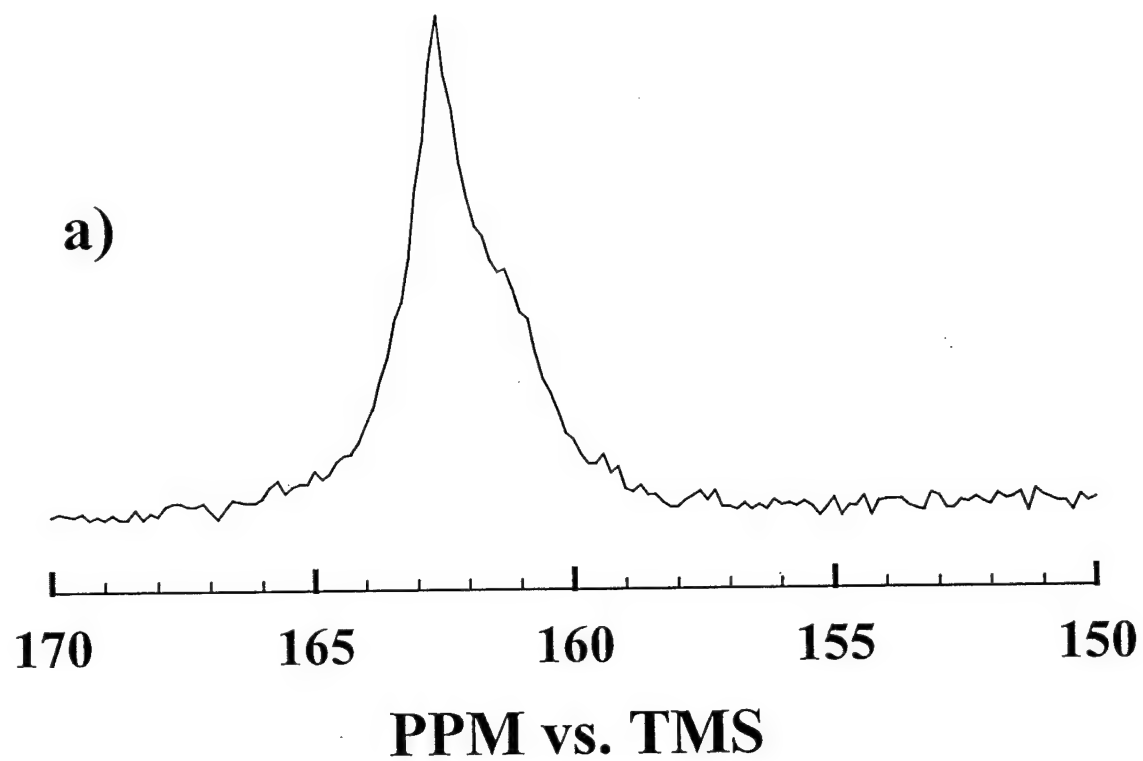
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14. Synthesis of the polymer using a different solvent system (50/50 THF/methanol) yields an XRD spectrum implicating two different rigid rod conformations. The XRD of these samples contain sharp peaks at 11.5 Å and 10.3 Å and broad bands centered at 4.5 Å and 3.0 Å. It is interesting to note that preparations of the polymer in mixed THF/methanol solvent precipitate polymer over longer periods of time in direct relation to the increasing

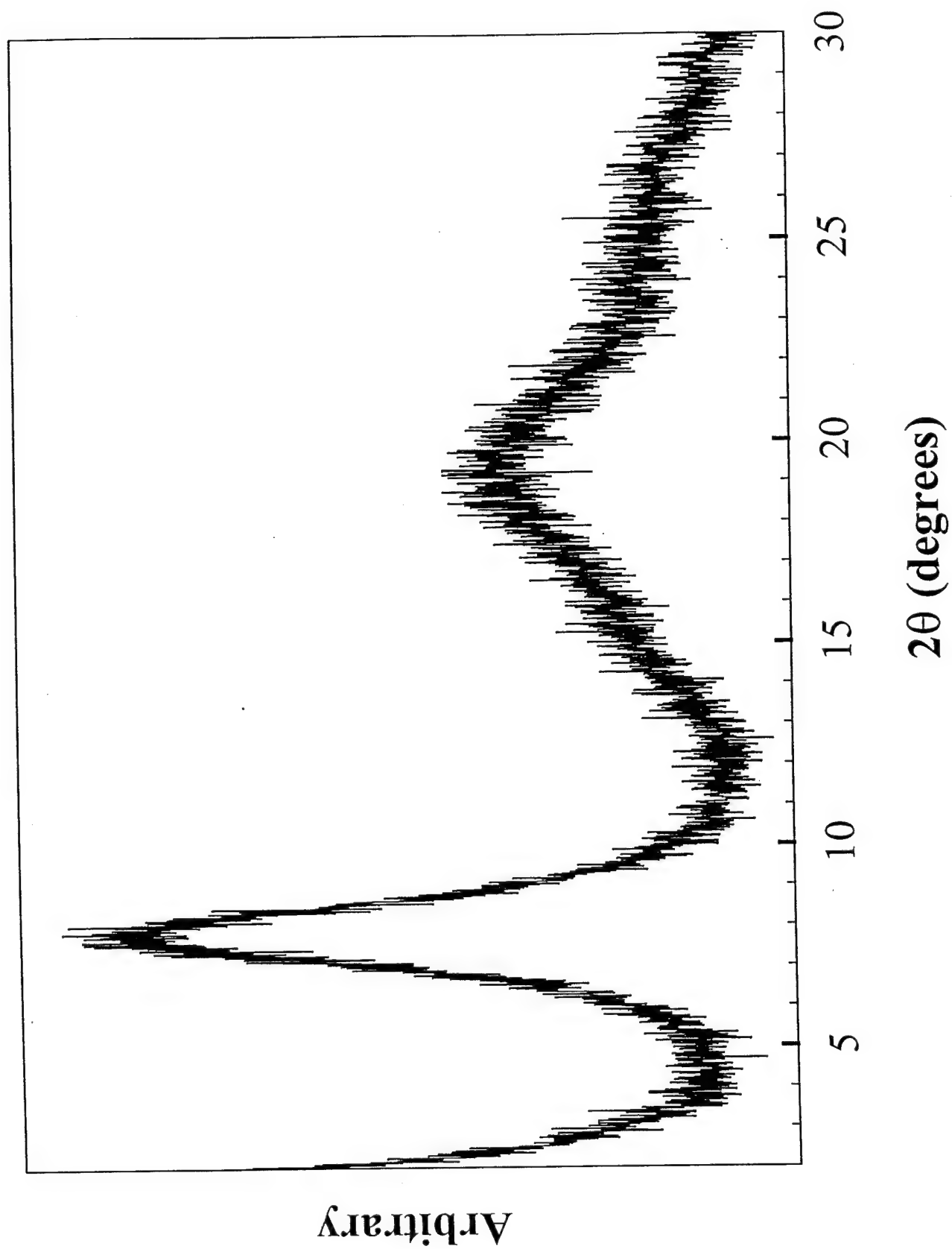
mole fraction of THF and yet the apparent number average molecular weight estimated by GPC of all of these "as prepared" samples is essentially the same. In contrast, a polymer prepared using butanol as the solvent had an apparent M_n about twice that of the polymers discussed in this paper.

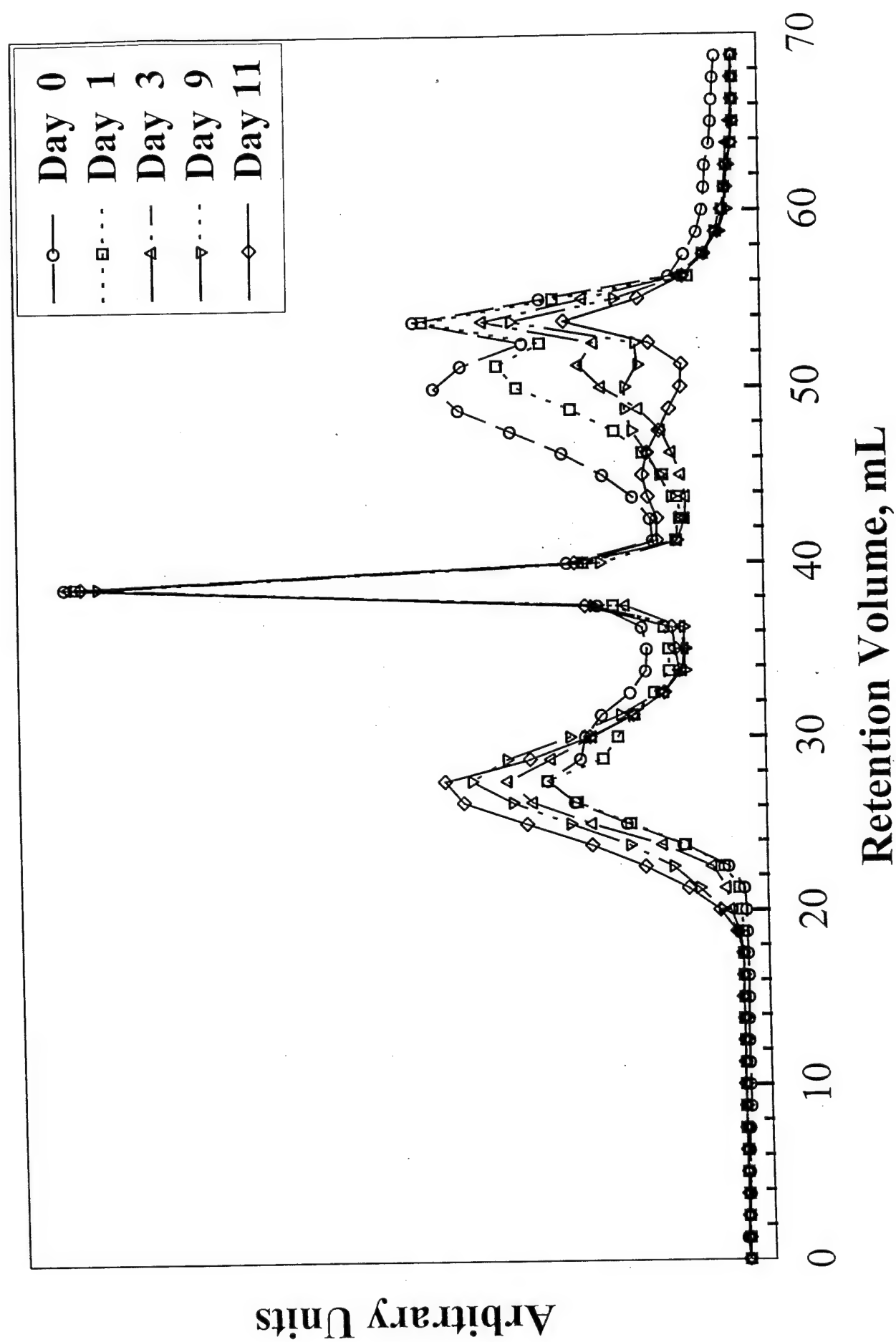
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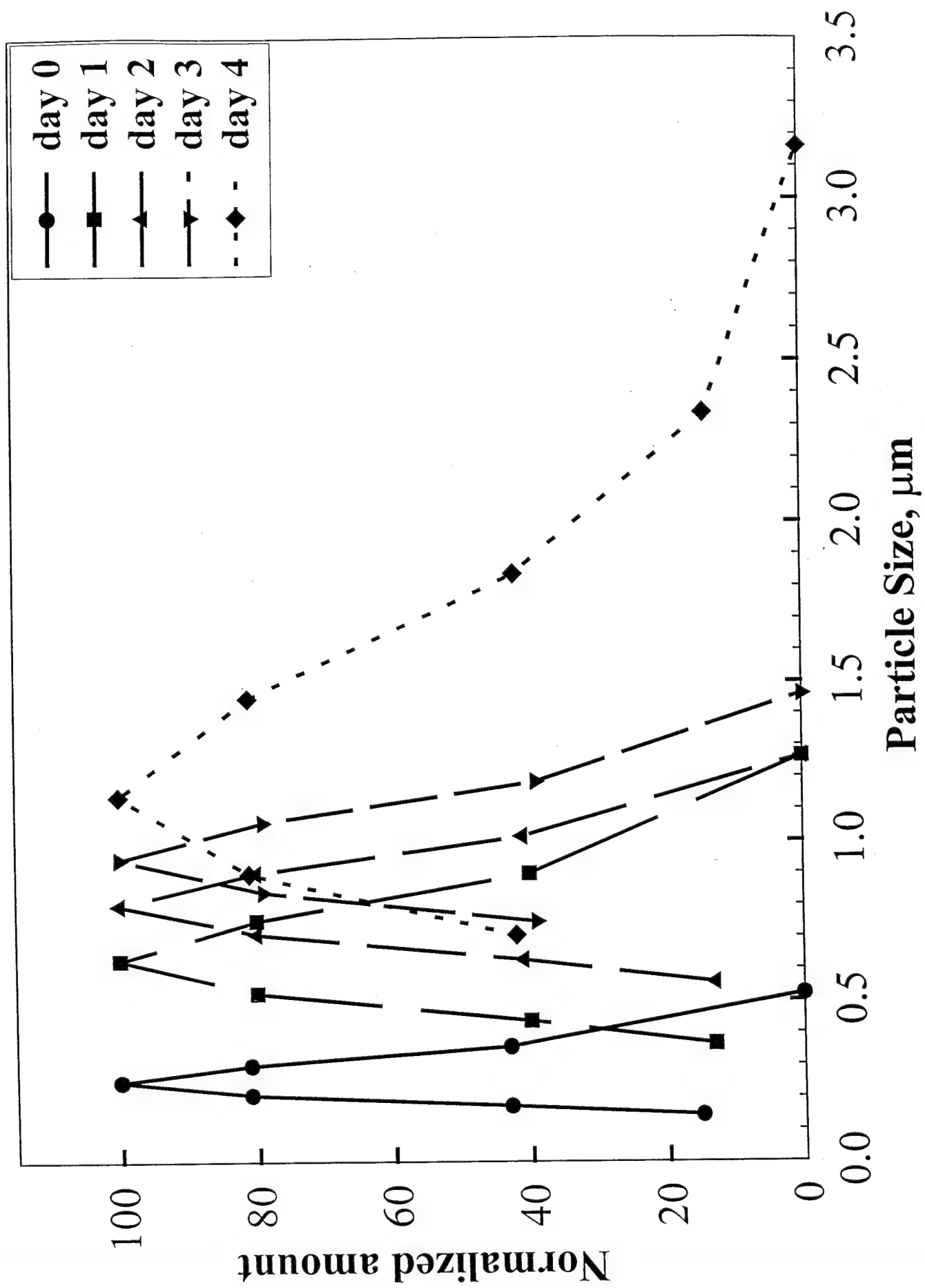
Figure Captions

- Figure 1 NMR spectra for the imine region of N- ϕ -PIM: a) ^{13}C and b) ^{15}N .
- Figure 2 XRD of the "as prepared" N- ϕ -PIM.
- Figure 3 Changes in the GPC of the polymer in THF solution as a function of time. The peak at about 39 mL is an internal standard used to calibrate the chromatogram.
- Figure 4 Particle size distributions as a function of time for the polymer in THF.
- Figure 5 XRD intensity data as a function of time.
- Figure 6 UV-vis spectrum of N- ϕ -PIM in acetonitrile solution. The dashed line is $\times 10$ of the solid line.
- Figure 7 Observed rate constant for the reaction of N- ϕ -PIM in THF solution as a function of initial concentration and at different temperatures.
- Figure 8 Possible structure of a polymer showing the three different types of imines observed in the NMR spectra.

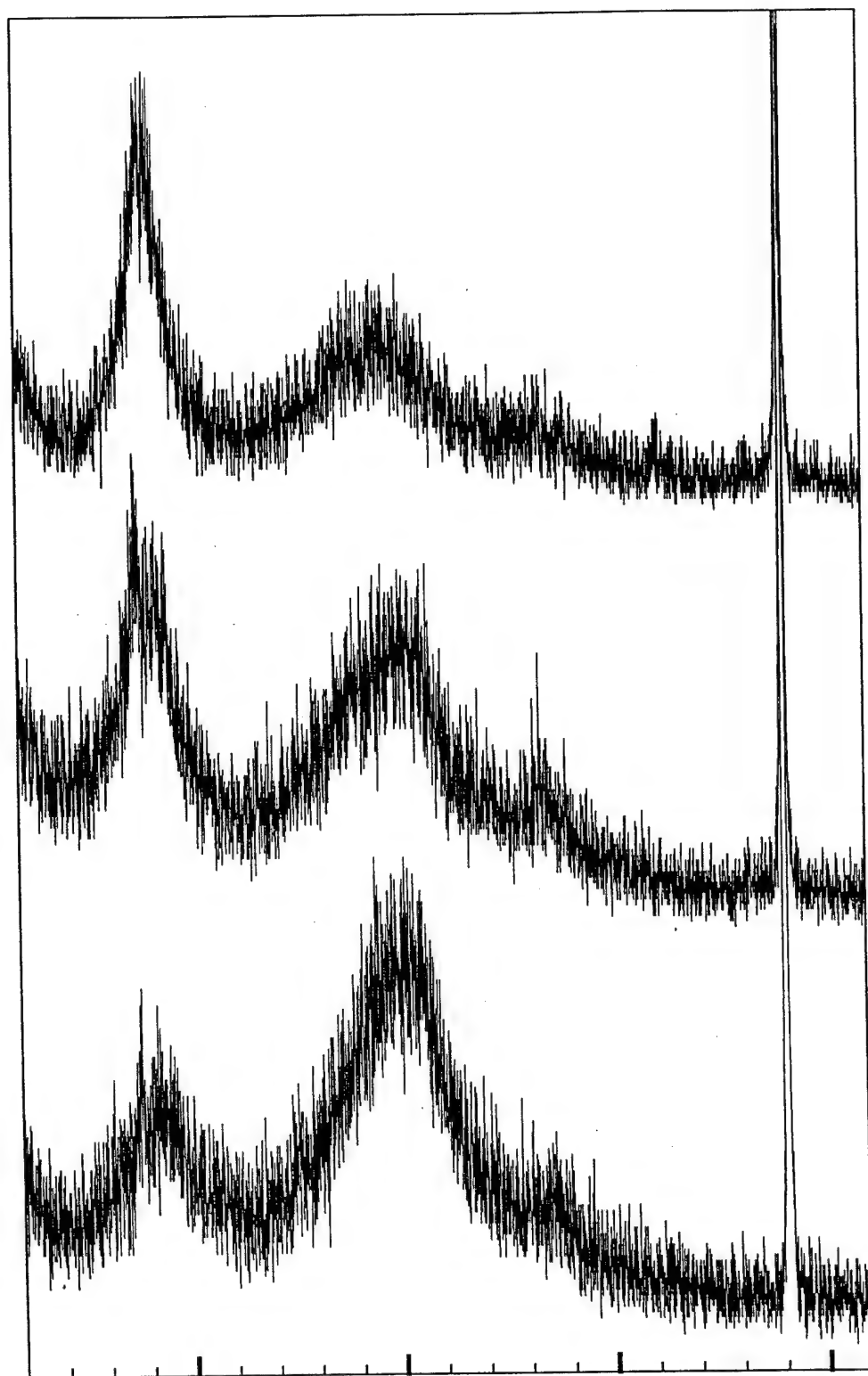








Arbitrary



1 hour

4 days

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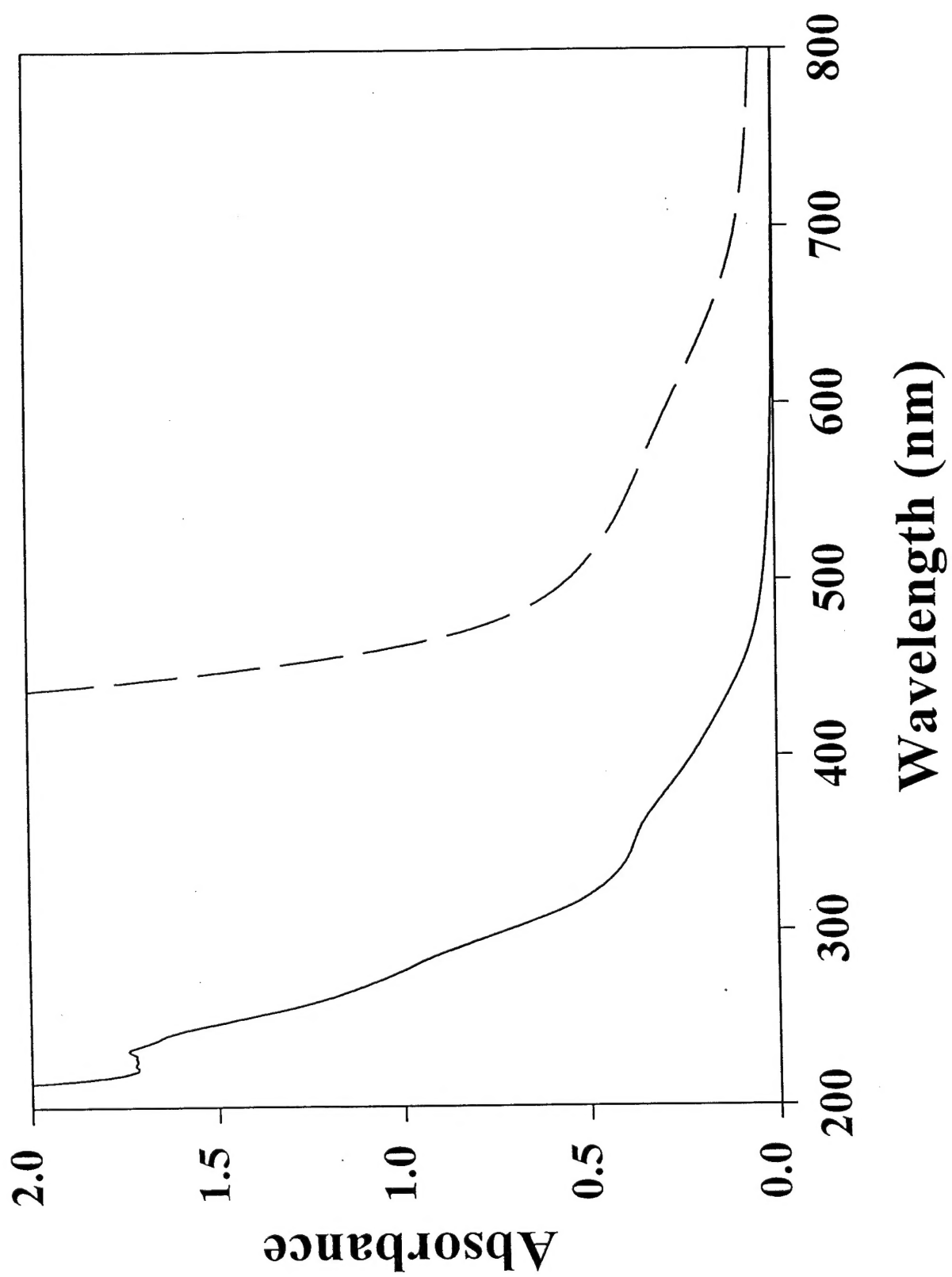
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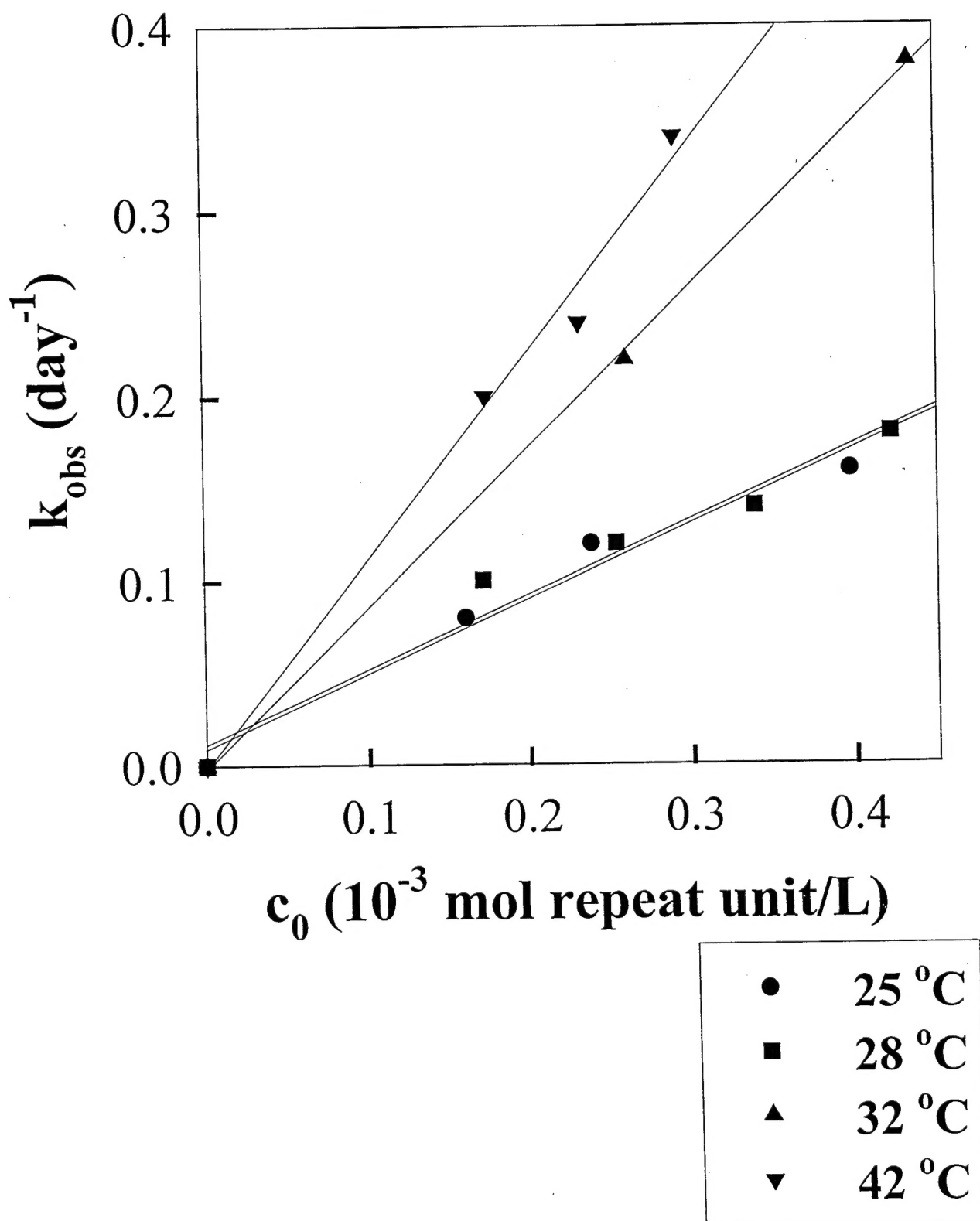
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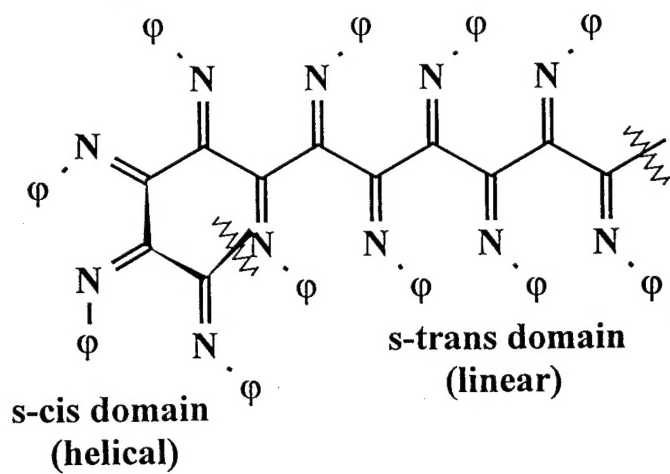
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2θ (degrees)





transition domain



List of Personnel

Rupendra Simlot - Postdoctoral Fellow
Misoo Kim - Master's Degree awarded 1994
Jiun-Tang Huang - Ph.D. Degree expected 1996
Jingxian Sun - Ph.D. Degree expected 1996

List of Publications

1. "The Solvent Sensitive Reaction of Phenyl Substituted Poly(iminomethylene)," J. Sun, J.-T. Huang, W. B. Euler, W. Rosen, *Proceedings of the Second International Conference on Intelligent Materials*, C. A. Rogers, G. G. Wallace, ed., Technomic Publishing Co., Lancaster, PA, **1994**, 1223-1229.
2. "Aggregation and Precipitation Phenomena in Poly(phenylisocyanide)," J.-T. Huang, J. Sun, W. B. Euler, W. Rosen, submitted to *Macromolecules*, **1995**.